Chapter 4

Diatomics in Molecules - DIM

In this chapter it is shown how the Diatomic in molecules method is applied to systems of dihalogens in a rare gas environment. First, the construction of the Hamiltonian is shown and in the subsequent section each part is discussed in detail, including derivation and application of the particular elements. The proper choice of the basis for the Hamiltonian is discussed, which is chosen in this work to consist of the Valence-Bond wave functions of the guest molecule. To this, all the other interactions are added, the halogen-argon interaction and the spin-orbit coupling. Here electron-hole dualism has to be taken into account, where the electron hole of the halogen's p-orbital is treated like a single electron, which will lead to a modification of the respective coupling elements.

4.1 Potentials for XY in Argon

The potentials for dihalogens in Argon were calculated using the Diatomics in Molecules (DIM) approach [7, 8, 9, 11, 73, 23, 75, 29, 39, 6, 12, 13, 14]. Here the total Hamiltonian of the system is built by taking into account all of the interactions of the system. These are the following:

1. interaction between the closed shell rare gas atoms, which are described by pair potentials

2. interaction between the atoms of the molecule, X and Y, including spin-orbit interaction

3. interaction between the open shell halogen atoms of the molecule and the argon atoms, respectively

From this the total Hamiltonian of the system results:

$$\hat{H}_{total} = \underbrace{H_{mol}^{XY} + V_{SO}^{XY}}_{XY} + \underbrace{\sum_{X,Y}\sum_k U_{(X,Y),k}^{DIM}\left(r_{(X,Y),k}, \gamma_{(X,Y),k}\right)}_{(X,Y)-Ar} + \underbrace{\sum_{k,l} V_{Ar_k-Ar_l}}_{Ar-Ar} \quad (4.1)$$

To develop the Hamiltonian, one has to accomplish the following steps

1. choose a basis for the Hamiltonian

   usually the molecular Hamiltonian in p_{-1}, p_0, p_{+1}-representation for each halogen atom is taken as basis. This has the advantage that the resulting matrix is diagonal with the eigenvalues of the free molecule (without spin-orbit coupling) as diagonal elements. The Hamiltonian becomes an $n \times n$ matrix where n equals the number of the wavefunctions. In the present case the Hamiltonian will consist of 36 wavefunctions and thus built a 36x36 matrix (see 1.1.3).

2. to this matrix all the other interactions are added and then by diagonalizing the eigenvalues of the system are achieved.

4.2 Wavefunctions

The strategy is to build first the wavefunctions of the free molecule without spin orbit coupling and then to add the coupling separately.
In this chapter the interhalogen ClF is taken as example for systems XY to show the general derivations of the method. The Valence Bond approach is used for creation of the wavefunctions. Here all the core electrons of the Cl and F atoms are ignored and only the valence electrons are taken into account.The corresponding configuration is $1s^2 2s^2 2p^5$ for the F atom and $1s^2 2s^2 2p^6 3s^2 3p^5$ for the Cl atom. The hole in the electronic configuration is equivalent, and therefore, treated like a single electron. This corresponds to the particle-hole dualism and leads to equivalent wave functions for the molecule. The only problem arises by treating the spin-orbit coupling of an electron configuration like p^5 as one like p^1, but this problem will be discussed later in Section 4.4.2.

4.2.1   Construction of the VB-wavefunctions

The electronic configuration of the F and Cl-atoms are, respectively:

F $(1s^2 2s^2 2p^5)$
Cl $(1s^2 2s^2 2p^6 3s^2 3p^5)$

Each atom has an angular momentum of l=1 with m_l=-1,0,1 and a spin of $\pm\frac{1}{2}$. This leads to six possible combinations for spin and angular momentum for each atom.

For the ClF molecule we get the possible projections for the total angular momentum:

$m_l(F)\backslash m_l(Cl)$	-1	0	1
-1	-2	-1	0
0	-1	0	1
1	0	1	2

$m_s(F)\backslash m_s(Cl)$	$\frac{1}{2}$	$-\frac{1}{2}$
$\frac{1}{2}$	1	0
$-\frac{1}{2}$	0	-1

To get a complete set of all possible combinations, we then will have 36 wavefunctions, thus a 36x36 matrix for the Hamiltonian. Construction of these wavefunctions is performed using ladder-operators for angular momentum and spin. First we have to determine good quantum numbers, which will only appear for commuting operators:

$$
\begin{aligned}
\text{H} &\quad &\quad &\rightarrow \text{E} \\
[H, S_z] &= &0 &\rightarrow M_S \\
[S_x, S_y] &= &-iS_z &\quad \text{and cyclic} \\
[H, L_z] &= &0 &\rightarrow M_L \\
[L_x, L_y] &= &-iL_z &\quad \text{and cyclic} \\
[H, S^2] &= &0 &\rightarrow S(S+1) \\
[H, L^2] &= &0 &\rightarrow L(L+1)
\end{aligned}
$$

The good quantum numbers without spin-orbit coupling are then L, M_L, S and M_S

With $[L_x, L_y] = -iL_z$ and cyclic, the ladder operators are defined as [1]:

$$L_+ = \frac{1}{\sqrt{2}}(L_x + iL_y) \tag{4.2}$$

$$L_- = \frac{1}{\sqrt{2}}(L_x - iL_y) \tag{4.3}$$

these operators can be used to construct new wavefunctions:

$$L_+ Y_{L,M_L} = \sqrt{L(L+1) - M_l(M_L + 1)} \hbar Y_{L,M_L+1} \tag{4.4}$$

$$L_- Y_{L,M_L} = \sqrt{L(L+1) - M_l(M_L - 1)} \hbar Y_{L,M_L-1} \tag{4.5}$$

and the same for the spin:

$$S_+ g(S, M_S) = \sqrt{S(S+1) + S_z(S_z - 1)} \hbar g(S, M_{S+1}) \tag{4.6}$$

$$S_- g(S, M_S) = \sqrt{S(S+1) - S_z(S_z - 1)} \hbar g(S, M_{S-1}) \tag{4.7}$$

Before applying these ladder operators, it is helpful to build a matrix consisting of the possible values of M_L and M_S and there tabulate all existing configurations:

		M_S	
	-1	0	1
2	1↓1↓	1↑1↓, 1↓1↑	1↑1↑
1	0↓1↓ 1↓0↓	0↑1↓, 0↓1↑ 1↑0↓, 1↓0↑	0↑1↑ 1↑0↑
0	-1↓1↓ 0↓0↓ 1↓-1↓	-1↓1↑, -1↑1↓ 0↓0↑, 0↑0↓ 1↓-1↑, 1↑-1↓	-1↑1↑ 0↑0↑ 1↑-1↑
-1	0↓-1↓ -1↓0↓	0↑-1↓, 0↓-1↑ -1↑0↓, -1↓0↑	0↑-1↑ -1↑0↑
-2	−1↓-1↓	-1↑-1↓, -1↓-1↑	-1↑-1↑

(M_L labels the rows on the left.)

where e.g. $1 \uparrow 1 \uparrow$ denotes the Slater-determinant with quantum numbers L=2, M_L=2, S=1, M_S=1. Then one unique configuration is taken (like L=2, S=1, M_L=2, M_S=1) and the ladder-operators are applied. For example, to get the configuration L=2, S=1, M_L=1, M_S=1 the lowering operator L_- is applied. Next, operating with the lowering operator on the configuration $|$L=2, M=1, S=1, S_z=1$\rangle$ will lead to the next configuration $|$L=2, M=0, S=1, S_z=1$\rangle$. By applying the raising and lowering ladder-operators for the spin the other columns are created. To make sure that the resulting wavefunctions are orthogonal to each other, the Schmidt algorithm for orthogonalization is taken into account. Finally these procedure is worked out until all configurations are determined.

For many-electron diatomic molecules, H commutes with the operator for the axial component of L, which has the possible values $M_L\hbar$ with $M_L = \sum_i m_{li}$. Thus for characterization of the appropriate states $\Lambda = |M_L|$ is used. E.g. $\Lambda = \Sigma, \Pi, \Delta$ for $|M_L|$=0, 1, 2, respectively [1].

4.2.2 Example

We start with a unique configuration:

$$
\begin{aligned}
|1 \uparrow 1 \uparrow\rangle &= \Psi_{L=2, M_L=2, S=1, S_z=1} \\
&\hat{=} \; {}^3\Delta \\
L_- \Psi_{2211} &= \sqrt{L(L+1) - M_L(M_L - 1)} \Psi_{2111} \\
&= \sqrt{2(2+1) - 2(2-1)} \Psi_{2111} \\
&= 2\Psi_{2111} \\
&\hat{=} \; 2{}^3\Pi
\end{aligned}
$$

$$
\begin{aligned}
L_- &= l_{1-} + l_{2-} \\
(l_{1-} + l_{2-})|1 \uparrow 1 \uparrow\rangle &= \sqrt{1 \cdot 2 - 1 \cdot 0}|0 \uparrow 1 \uparrow\rangle \\
&\quad + \sqrt{1 \cdot 2 - 1 \cdot 0}|1 \uparrow 0 \uparrow\rangle \\
&= \sqrt{2}(|0 \uparrow 1 \uparrow\rangle + |1 \uparrow 0 \uparrow\rangle)
\end{aligned}
$$

Using the Slater determinants this can be written as shown below, where in our case index a belongs to the fluorine atom and index b belongs to the chlorine atom:

$$
|0 \uparrow 1 \uparrow\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} p_{a_0}\alpha(1) & p_{b_+}\alpha(1) \\ p_{a_0}\alpha(2) & p_{b_+}\alpha(2) \end{vmatrix} = \frac{1}{\sqrt{2}}(p_{a_0}p_{b_+} - p_{b_+}p_{a_0})\alpha\alpha
$$

$$
|1 \uparrow 0 \uparrow\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} p_{a_+}\alpha(1) & p_{b_0}\alpha(1) \\ p_{a_+}\alpha(2) & p_{b_0}\alpha(2) \end{vmatrix} = \frac{1}{\sqrt{2}}(p_{a_+}p_{b_0} - p_{b_0}p_{a_+})\alpha\alpha
$$

$$
(l_{1-} + l_{2-})|1 \uparrow 1 \uparrow\rangle = \frac{\sqrt{2}}{\sqrt{2}}[((p_{a_0}p_{b_+} - p_{b_+}p_{a_0}) + (p_{a_+}p_{b_0} - p_{b_0}p_{a_+}))\alpha\alpha]
$$

$$
L_- \Psi_{2211} = 2\Psi_{2111}
$$

$$
\Rightarrow 2 \cdot \Psi_{2111} = [((p_{a_0}p_{b_+} - p_{b_+}p_{a_0}) + (p_{a_+}p_{b_0} - p_{b_0}p_{a_+}))\alpha\alpha]
$$

$$
{}^3\Pi = \Psi_{2111} = \frac{1}{2}[((p_{a_0}p_{b_+} - p_{b_+}p_{a_0}) + (p_{a_+}p_{b_0} - p_{b_0}p_{a_+}))\alpha\alpha]
$$

	Spatial part of wf	M_L	M_S
$^1\Sigma$ (first)	$\frac{1}{\sqrt{2}}(a_0 b_0 + b_0 a_0)$	0	0 (singlet)
$^1\Sigma$ (second)	$\frac{1}{2}((a_+ b_- + b_- a_+) + (a_- b_+ + b_+ a_-))$	0	0 (singlet)
$^1\Sigma^-$	$\frac{1}{2}((a_+ b_- + b_- a_+) - (a_- b_+ + b_+ a_-))$	0	0 (singlet)
$^1\Pi$(first)	$\frac{1}{2}((a_0 b_- + b_- a_0) - (a_- b_0 + b_0 a_-))$	-1	0 (singlet)
	$\frac{1}{2}((a_0 b_+ + b_+ a_0) - (a_+ b_0 + b_0 a_+))$	1	0 (singlet)
$^1\Pi$ (second)	$\frac{1}{2}((a_0 b_- + b_- a_0) + (a_- b_0 + b_0 a_-))$	-1	0 (singlet)
	$\frac{1}{2}((a_0 b_+ + b_+ a_0) + (a_+ b_0 + b_0 a_+))$	1	0 (singlet)
$^1\Delta$	$\frac{1}{\sqrt{2}}(a_- b_- + b_- a_-)$	-2	0 (singlet)
	$\frac{1}{\sqrt{2}}(a_+ b_+ + b_+ a_+)$	2	0 (singlet)
$^3\Sigma$ (first)	$\frac{1}{\sqrt{2}}(a_0 b_0 - b_0 a_0)$	0	-1,0,1 (triplet)
$^3\Sigma$ (second)	$\frac{1}{2}((a_+ b_- - b_- a_+) + (a_- b_+ - b_+ a_-))$	0	-1,0,1 (triplet)
$^3\Sigma$ (third)	$\frac{1}{2}((a_+ b_- - b_- a_+) - (a_- b_+ - b_+ a_-))$	0	-1,0,1 (triplet)
$^3\Pi$(first)	$\frac{1}{2}((a_0 b_- - b_- a_0) + (a_- b_0 - b_0 a_-))$	-1	-1,0,1 (triplet)
	$\frac{1}{2}((a_0 b_+ - b_+ a_0) + (a_+ b_0 - b_0 a_+))$	1	-1,0,1 (triplet)
$^3\Pi$ (second)	$\frac{1}{2}((a_0 b_- - b_- a_0) - (a_- b_0 - b_0 a_-))$	-1	-1,0,1 (triplet)
	$\frac{1}{2}((a_0 b_+ - b_+ a_0) - (a_+ b_0 - b_0 a_+))$	1	-1,0,1 (triplet)
$^3\Delta$	$\frac{1}{\sqrt{2}}(a_- b_- - b_- a_-)$	-2	-1,0,1 (triplet)
	$\frac{1}{\sqrt{2}}(a_+ b_+ - b_+ a_+)$	2	-1,0,1 (triplet)

Table 4.1: *Valence-bond wavefunctions of dihalogens*

These wavefunctions have the general form

$$\Psi_i(1,2) \;=\; \sum_{kl} c_{ikl}\Phi_k(1)\Phi_l(2) \tag{4.8}$$

The application of the general form in eq. 4.8 on the wavefunctions is shown in

two examples:

$$
\begin{aligned}
{}^1\Sigma(1,2) &= \frac{1}{\sqrt{2}}(a_0(1)b_0(2) + b_0(1)a_0(2))\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2)) \\
&= \frac{1}{\sqrt{2}}(a_0(1)\alpha(1)b_0(2)\beta(2) + b_0(1)\alpha(1)a_0(2)\beta(2) - a_0(1)\beta(1)b_0(2)\alpha(2) \\
&\quad - b_0(1)\beta(1)a_0(2)\alpha(2) \\
{}^3\Pi(1,2) &= \frac{1}{2}((a_0b_+ - b_+a_0) - (a_+b_0 - b_0a_+))(\beta\beta) \\
&= \frac{1}{2}(a_0(1)\beta(1)b_+(2)\beta(2) - b_+(1)\beta(1)a_0(2)\beta(2) - a_+(1)\beta(1)b_0(2)\beta(2) \\
&\quad + b_0(1)\beta(1)a_+(2)\beta(2))
\end{aligned}
$$

4.3   Interaction with Argon
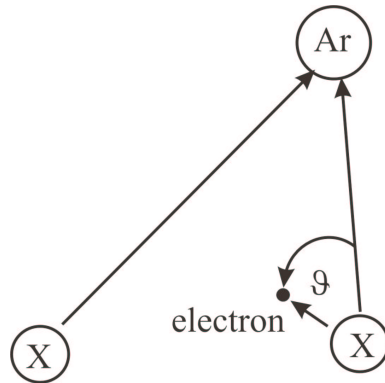
Figure 4.1: *Halogen-argon interaction*

To describe the interaction of the closed shell atoms and the open shell atoms first order perturbation theory is used [2], introducing the perturbation of the atomic energy levels of by rare-gas neighbours. All core electrons of the halogens are assumed to be unaffected by the rare gas atoms. The interaction is calculated regarding the hole in the electron configuration of the halogen atom. The resulting Hamiltonian for this system is:

$$
\hat{H} = \hat{H}_a(r) + \sum_k V(r, R_k) \tag{4.9}
$$

With r being the position vector of the electron hole and $V(r,R_k)$ the interaction potential between halogen atom and a rare gas atom with position vector R_k,

where the sum over all argon atoms is built.

The basis of the DIM-Hamiltonian consists of wavefunctions of the type $|p_{ai}p_{bj}>$ which are arranged in blocks with same spin.

$$< p_{ai}p_{bj}| \sum_i V_{ai} + \sum_i V_{bi}|p_{ak}p_{bl} >=$$

$$< p_{ai}| \sum_i V_{ai}|p_{ak} >< p_{bj}|p_{bl} >$$

$$+ < p_{ai}|p_{ak} >< p_{bj}| \sum_i V_{bi}|p_{bl} >$$

$$< p_{ai}| \sum_i V_{ai}|p_{ak} >= \sum_i < p_{ai}|V_{ai}|p_{ak} > \qquad (4.10)$$

with a= F, b=Cl and i=Ar$_i$. Further, the interaction potential V_{X-Rg} is expanded in Legendre polynomials:

$$V_{X-Rg}(\vartheta_1, ...\vartheta_k, R_1, ...R_k) = \sum_k \sum_{L=0}^{\infty} V_L(R_k)P_L(cos\vartheta_k) \qquad (4.11)$$

where ϑ_k denotes the angle between atom k and the electron(hole) centered at r (see Fig. 4.1).This orientation angle is thus, within the DIM-model, the only electronic degree of freedom [79]. For a system like a halogen atom l=1. So for the spherical harmonics all odd terms will vanish by integration and all terms higher L=2 won't appear due to l=1, see below. The present basis for the electron(hole) will be $|p_{am_i}>= |p_{a,(m=-1,0,1)}>= |p_{a,m_l}>$

$$V_{X-Rg}(\vartheta_1, ...\vartheta_k, R_1, ...R_k) = V_0(R_k) + V_2(R_k)P_2(cos\vartheta_k) \qquad (4.12)$$

$$V_{m_l,m_l'} \equiv < p_{a,m_l}|V_0(R_k) + V_2(R_k)P_2(cos\vartheta_k)|p_{a,m_l'} >$$

$$= V_0(R_k) < p_{a,m_l}|p_{a,m_l'} > +V_2(R_k) < p_{a,m_l}|P_2(cos\vartheta_k)|p_{a,m_l'} > \qquad (4.13)$$

$$P_L(cos\vartheta_k) = \sqrt{\frac{4\pi}{2L+1}} \sum_M Y_{L,M}(\vartheta, \varphi)Y_{L,M}^*(\vartheta_k, \varphi_k) \qquad (4.14)$$

Generally, as shown e.g. by Apkarian and Schwentner [19] the matrix elements are:

$$V_{m_l,m_l'} = \sum_k \sum_{L=0,2} \frac{4\pi}{2L+1} < Y_{l,m_l'}| \sum_{M=-L}^{L} Y_{LM}|Y_{l,m_l} > V_L(R_k)Y_{LM}^*(\vartheta_k, \varphi_k) \,(4.15)$$

where l=1 for the p-orbitals. The quantum numbers for the matrix element

$$\begin{pmatrix} l & L & l \\ m_l & M & m_l' \end{pmatrix} \equiv < Y_{l,m_l'}|Y_{LM}|Y_{l,m_l} > \tag{4.16}$$

(Clebsch-Gordan coefficients) satisfy the triangle relation

$$m_{l'} + M + m_l = 0 \tag{4.17}$$

$$l_1 + l_2 \geq L \geq |l_1 - l_2| \tag{4.18}$$

For $l_1=l_2=1$, therefore, only the terms L=0 and L=2 contribute to the sum $\sum_{L=0}^{\infty}$ V_0 and V_2 describe the isotropic and anisotropic part of the potential,respectively, and can be represented by the pair potentials V_Σ and V_Π [3, 5].

$$V_0(R_k) = \frac{1}{3}(V_\Sigma(R_k) + 2V_\Pi(R_k)) \tag{4.19}$$

$$V_2(R_k) = \frac{5}{3}(V_\Sigma(R_k) - V_\Pi(R_k)) \tag{4.20}$$

4.4 Spin-Orbit Coupling

Spin-Orbit coupling is an important factor for diatomic molecules, both for the energetics and for the dynamics of the system. For dihalogens in general there will appear the problem of the particle-hole dualism, where the hole in the electronic configuration will lead to the same spin-orbit coupling term as a single electron but with opposite sign for the values of the spin-orbit coupling, as referred to in section 4.4.2. To give a consistent presentation, first the principles of spin-orbit coupling will be discussed. The given results will then be used for the system ClF.

A long, straight conductor generates a magnetic field whose flux lines lie perpendicular to the flow of charge and build a right hand oriented system. This is described by Faraday's rule:

$$\vec{B} = \frac{1}{c^2}\vec{v}_{Ze} \times \vec{E}_{Ze} \tag{4.21}$$

with velocity $\vec{v}$. The interaction of the dipole moment associated with the spin of the electron with this magnetic field is given by

$$V_{SO} = -\vec{\mu}_s\vec{B} \quad with \quad \vec{\mu}_s = -g_e\frac{e}{2m_e}\vec{s} \tag{4.22}$$
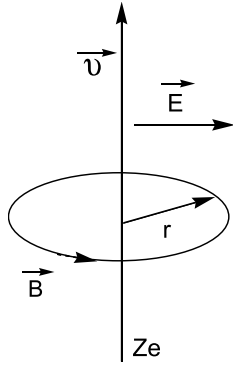
Figure 4.2: *Magnetic field generated by a straight conductor*

with g_e being the gyromagnetic constant derived by Dirac's relativistic treatment of the electron and has a value of ≈ 2, and $\vec{s}$ means the electronic spin angular momentum.

Likewise, for a nuclear spin the spin-orbit coupling is given by:

$$V_{SO} = -\vec{\mu}_I \vec{B} \quad with \quad \vec{\mu}_I = +g_I \frac{Ze}{2M} \vec{I} \tag{4.23}$$

There are several interactions that have to be discussed:

- electron spin - nuclear motion

- electron spin - other electron motion

- nuclear spin - electron motion

- nuclear spin - nuclear motion

First we derive the expression for the first interaction. From these, the expressions for the other interactions follow by analogy:

- electron spin - nuclear motion

    First we have to regard that the velocity and angular momentum of the nucleus corresponds to the negative velocity and angular momentum of the electron, taking the nucleus or the electron as point of view, respectively. For slow motion Coulomb's law can be applied:

$$\Phi_{Coulomb} = -\frac{Ze}{4\pi\varepsilon_0 r} \tag{4.24}$$

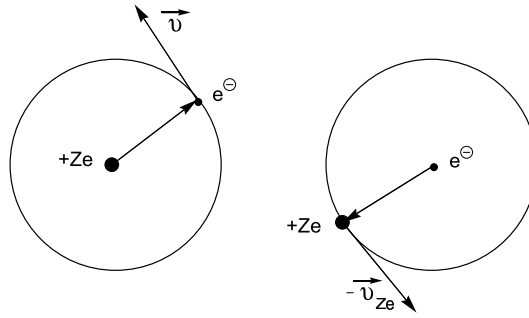Figure 4.3: *Velocity and angular momentum, taking the nucleus or electron as a point of view*

with

$$\vec{E}_{+Ze} = \nabla\Phi = \frac{Ze}{4\pi\varepsilon_0 r^2}\frac{\vec{r}}{r} \tag{4.25}$$

So the magnetic field can be derived as:

$$\begin{aligned}
\vec{B} &= \frac{1}{c^2}(\vec{v}_{Ze} \times \vec{E}_{Ze}) \\
&= -\frac{1}{c^2}(\vec{E}_{Ze} \times \vec{v}_{Ze}) \\
&= \frac{1}{c^2}(\vec{E}_{Ze} \times \vec{v}_e) \tag{4.26}
\end{aligned}$$

$$\tag{4.27}$$

with

$$\begin{aligned}
\vec{E}_{Ze} &= \frac{Ze}{4\pi\varepsilon_0 r^3}\vec{r} \tag{4.28} \\
\vec{B} &= \frac{Ze}{c^2 4\pi\varepsilon_0 r^3}(\vec{r} \times \vec{v}) \quad /\cdot\frac{m_e}{m_e} \\
&= \frac{Ze}{c^2 4\pi\varepsilon_0 r^3 m_e}(\vec{r} \times m_e\vec{v}) \\
&= \frac{Ze}{c^2 4\pi\varepsilon_0 r^3 m_e}\vec{l} \tag{4.29} \\
\vec{l} &= \vec{r} \times \vec{p} \tag{4.30}
\end{aligned}$$

The dipole of the electron due to the spin has potential energy of orientation

in this magnetic field given by:

$$
\begin{aligned}
V_{SO} &= -\vec{\mu_S}\vec{B} \\
&= (-g_e \frac{e}{2m_e}\vec{s})(+\frac{Ze}{4\pi\varepsilon_0 c^2 m_e r^3}\vec{l}) \\
&= -\underbrace{\frac{g_e}{8\pi\varepsilon_0 c^2 m_e}}_{A}\frac{Ze^2}{r^3}\vec{s}\vec{l}
\end{aligned}
\tag{4.31}
$$

By analogy, the other interactions are given as follows:

- electron spin - other electron motion

$$
V_{SO} = -\underbrace{\frac{g_e}{8\pi\varepsilon_0 c^2 m_e}}_{A}\frac{e^2}{r^3}\vec{s}\vec{l}
\tag{4.32}
$$

- nuclear spin - electron motion

$$
V_{SO} = \frac{g_I}{8\pi\varepsilon_0 c^2 M}\frac{Ze^2}{r^3}\vec{I}\vec{l}
\tag{4.33}
$$

This term can be neglected because of the dependence on $\frac{1}{M}$.

- nuclear spin - nuclear motion

$$
V_{SO} = \frac{g_I}{8\pi\varepsilon_0 c^2 M}\frac{Z^2 e^2}{r^3}\vec{I}\vec{l}
\tag{4.34}
$$

Likewise this term can be neglected because of the dependence on $\frac{1}{M}$.

So the total interaction can be written as

$$
\begin{aligned}
V_{SO} = A \cdot [&- \underbrace{\sum_{ia}\sum_{ja}\frac{e^2}{r_{ij}^3}\vec{s_j}\vec{l_i}}_{located\ at\ a} - \underbrace{\sum_{ib}\sum_{jb}\frac{e^2}{r_{ij}^3}\vec{s_j}\vec{l_i}}_{located\ at\ b} \\
&- \sum_{ia}\sum_{jb}\frac{e^2}{r_{ij}^3}\vec{s_j}\vec{l_i} - \sum_{ib}\sum_{ja}\frac{e^2}{r_{ij}^3}\vec{s_j}\vec{l_i} \\
&+ \underbrace{\sum_{j}\frac{Z_b e^2}{r_{jb}^3}\vec{s_j}\vec{l_j}}_{on\ b} + \underbrace{\sum_{i}\frac{Z_a e^2}{r_{ia}^3}\vec{s_i}\vec{l_i}}_{on\ a} \\
&+ \underbrace{\sum_{ib}\frac{Z_b e^2}{r_{ib}^3}\vec{s_i}\vec{l_i}}_{on\ a} + \underbrace{\sum_{ja}\frac{Z_a e^2}{r_{ja}^3}\vec{s_j}\vec{l_j}}_{on\ b}]
\end{aligned}
\tag{4.35}
$$

with

$$A = \frac{g_e}{8\pi\varepsilon_0 c^2 m_e}$$ (4.36)

As a consequence, the Spin-Orbit coupling is split into three parts:

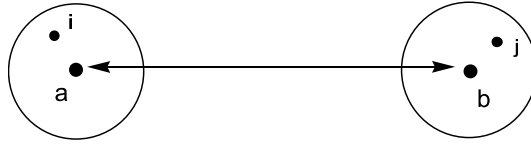$$V_{SO} = V_{SO,a} + V_{SO,b} + V_{SO,a,b}$$ (4.37)

Figure 4.4: *Distances between atom a and atom b with electron i,j, respectively.*

where $V_{SO,a}$ and $V_{SO,b}$ are the spin-orbit interactions within atoms a and b, whereas $V_{SO,a,b}$ depends on the distance between atoms a and b. Asymptotically, $r_{ij} \approx r_{ab}$, $r_{aj} \approx r_{ab}$, $r_{bi} \approx r_{ab}$, thus $V_{SO,ab} \propto \frac{1}{r_{ab}^3}$. The asymptotic behaviour of V_{SO} is illustrated in Fig. 4.5.
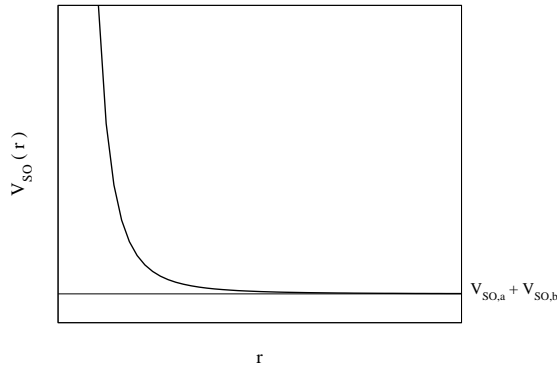

Figure 4.5: *Asymptotic behaviour of the spin-orbit coupling V_{SO}.*

Neglecting the interaction between electrons and nuclei located at different atoms, the spin-orbit coupling reduces to

$$V_{SO} \approx -\underbrace{\sum_i \sum_j \frac{e^2}{r_{ij}^3} \vec{s}_i \vec{l}_j}_{a} - \underbrace{\sum_i \sum_j \frac{e^2}{r_{ij}^3} \vec{s}_i \vec{l}_j}_{b} + \underbrace{\sum_i \frac{Z_a e^2}{r_{ai}^3} \vec{s}_i \vec{l}_i}_{a} + \underbrace{\sum_j \frac{Z_b e^2}{r_{bj}^3} \vec{s}_j \vec{l}_j}_{b}$$

$$(4.38)$$

This is an approximation, since for values of $r_{ab} < \infty$ there must be a correction term proportional $\frac{1}{r_{ab}^3}$. Neglecting this dependence, the Spin-Orbit coupling depends on just the contributions from the individual atoms [6]:

$$V_{SO} \approx V_{SO,a} + V_{SO,b} \qquad (4.39)$$

$$V_{SO} \approx \Delta_a \vec{l}_a \vec{s}_a + \Delta_b \vec{l}_b \vec{s}_b \qquad (4.40)$$

with

$$\Delta_a = \frac{g_e}{8\pi m_e^2 \varepsilon_0 c^2} \left[-\sum_i \sum_j \langle \frac{e^2}{r_{ij}^3} \rangle + \sum_i \langle \frac{Z_a e^2}{r_{ai}^3} \rangle \right] \qquad (4.41)$$

These so called spin-orbit coupling constant Δ_a, Δ_b are atom-specific constants which can be measured spectroscopically. The SO-constants for F (0.0501 eV) and Cl (0.109 eV) are taken from [22, 6]

4.4.1 Representation of Spin-orbit coupling in the basis of the model Hamiltonian

To add spin-orbit interactions to the Hamiltonian, $\mathbf{ls} = l_x s_x + l_y s_y + l_z s_z$ has to be presented in the basis p_{-1}, p_0, p_1 located at halogen atoms a (F) or b (Cl).

The matrix elements for the atomic wavefunctions are derived as follows, starting with the matrix representing l_z :

$$\mathbf{l_z} = \begin{pmatrix} \langle p_{-1}|l_z|p_{-1}\rangle & \langle p_{-1}|l_z|p_0\rangle & \langle p_{-1}|l_z|p_1\rangle \\ \langle p_0|l_z|p_{-1}\rangle & \langle p_0|l_z|p_0\rangle & \langle p_0|l_z|p_1\rangle \\ \langle p_2|l_z|p_{-1}\rangle & \langle p_1|l_z|p_0\rangle & \langle p_1|l_z|p_1\rangle \end{pmatrix} \qquad (4.42)$$

Using

$$l_z|\Psi_{l,m_l}\rangle = m_l\Psi_{l,m_l} \tag{4.43}$$

the matrix elements can be worked out:

$$\langle p_{-1}|l_z|p_{-1}\rangle = \langle p_{-1}| - p_{-1}\rangle = -1 \tag{4.44}$$

$$\langle p_0|l_z|p_0\rangle = \langle p_0|0 \cdot p_0\rangle = 0 \tag{4.45}$$

$$\langle p_1|l_z|p_1\rangle = \langle p_1|p_1\rangle = 1 \tag{4.46}$$

All the mixed terms vanish because of orthogonality, for example:

$$\langle p_0|l_z|p_{-1}\rangle = \langle p_0| - p_{-1}\rangle = 0$$

and so we get for the presentation of l_z in the basis p_{-1}, p_0, p_1:

$$\mathbf{l_z} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{4.47}$$

For the terms $l_x s_x$ and $l_y s_y$, l_x and l_y and similarly s_x and s_y for the spinfunction ω are worked out by ladder-operators ([1, 15] , see chapter 4.2):

$$l_x = -\frac{1}{\sqrt{2}}(l_{+1} - l_{-1}) \tag{4.48}$$

$$l_y = \frac{i}{\sqrt{2}}(l_{+1} + l_{-1}) \tag{4.49}$$

$$s_x = -\frac{1}{\sqrt{2}}(s_{+1} - s_{-1}) \tag{4.50}$$

$$s_y = \frac{i}{\sqrt{2}}(s_{+1} + s_{-1}) \tag{4.51}$$

$$\tag{4.52}$$

and therefore:

$$\mathbf{l_x s_x} + \mathbf{l_y s_y} = -l_{+1}s_{-1} - l_{-1}s_{+1} \tag{4.53}$$

Using the relations:

$$l_{+1}|\Psi_{l,m_l}\rangle = -\sqrt{\frac{1}{2}[l(l+1) - m_l(m_l+1)]}|\Psi_{l,m_l+1}\rangle \qquad (4.54)$$

$$l_{-1}|\Psi_{l,m_l}\rangle = +\sqrt{\frac{1}{2}[l(l+1) - m_l(m_l-1)]}|\Psi_{l,m_l-1}\rangle \qquad (4.55)$$

for ladder operators, the matrix elements of $\mathbf{l_x}$ and $\mathbf{l_y}$, e.g., are evaluated as follows:

$$\langle p_0|l_x|p_0\rangle = -\frac{1}{\sqrt{2}}\left(\langle p_0|l_+|p_0\rangle - \langle p_0|l_-|p_0\rangle\right)$$

$$l_+|p_0\rangle = -\sqrt{\frac{1}{2}[(1(1+1) - 0(0+1)]}|p_1\rangle$$

$$\langle p_0|l_+|p_0\rangle = -\langle p_0|p_1\rangle$$

$$= 0$$

$$l_-|p_0\rangle = \sqrt{\frac{1}{2}[1(1+1) - 0(0-1)]}|p_{-1}\rangle$$

$$\langle p_0|l_-|p_0\rangle = \langle p_0|p_{-1}\rangle$$

$$= 0$$

$$\Rightarrow \langle p_0|l_x|p_0\rangle = 0$$

A second example gives a value for the matrix element:

$$\langle p_0|l_x|p_{-1}\rangle = -\frac{1}{\sqrt{2}}\left(\langle p_0|l_+|p_{-1}\rangle - \langle p_0|l_-|p_{-1}\rangle\right)$$

$$l_+|p_{-1}\rangle = -\sqrt{\frac{1}{2}[1(1+1) - (-1)(-1+1)]}|p_0\rangle$$

$$= -|p_0\rangle$$

$$\langle p_0|l_+|p_{-1}\rangle = -\langle p_0|p_0\rangle$$

$$= -1$$

$$l_-|p_{-1}\rangle = \sqrt{\frac{1}{2}[1(1+1) - (-1)(-1-1)]}\text{``}|p_{-2}\rangle\text{''}$$

$$= 0$$

$$\Rightarrow \langle p_0|l_x|p_{-1}\rangle = \frac{1}{\sqrt{2}}$$

so we finally arrive at the representation of l_x and l_y in p_{-1}, p_0, p_1 basis:

$$\mathbf{l_x} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \tag{4.56}$$

$$\mathbf{l_y} = \frac{i}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} \tag{4.57}$$

The same procedure applied to the spin yields s_x and s_y in terms of ladder-operators s_+ and s_-:

$$\mathbf{s_x} = -\frac{1}{\sqrt{2}}(s_+ - s_-) \tag{4.58}$$

$$\mathbf{s_y} = \frac{i}{\sqrt{2}}(s_+ + s_-) \tag{4.59}$$

For these ladder-operators the same relations as for the spatial part are valid:

$$s_+|\Psi_{s,s_z}\rangle = -\sqrt{\frac{1}{2}[s(s+1) - s_z(s_z+1)]}|\Psi_{s,s_z+1}\rangle \tag{4.60}$$

$$s_-|\Psi_{s,s_z}\rangle = -\sqrt{\frac{1}{2}[s(s+1) - s_z(s_z-1)]}|\Psi_{s,s_z-1}\rangle \tag{4.61}$$

, thus

$$s_+|\beta\rangle = -\sqrt{\frac{1}{2}[\frac{1}{2}(\frac{1}{2}+1) - (-\frac{1}{2})(-\frac{1}{2}+1)]}|\alpha\rangle$$

$$= -\frac{1}{\sqrt{2}}|\alpha\rangle$$

$$s_-|\beta\rangle = \sqrt{\frac{1}{2}[\frac{1}{2}\left(\frac{1}{2}+1\right) - \left(-\frac{1}{2}\right)\left(-\frac{1}{2}-1\right)]}|\beta-1\rangle$$

$$= 0$$

$$s_+|\alpha\rangle \;=\; -\sqrt{\frac{1}{2}[\frac{1}{2}(\frac{1}{2}+1)-(\frac{1}{2})(\frac{1}{2}+1)]}|\alpha+1\rangle$$

$$=\;0$$

$$s_-|\alpha\rangle \;=\; \sqrt{\frac{1}{2}\left[\frac{1}{2}\left(\frac{1}{2}+1\right)-\left(-\frac{1}{2}\right)\left(-\frac{1}{2}+1\right)\right]}|\beta\rangle$$

$$=\;\frac{1}{\sqrt{2}}|\beta\rangle$$

So for $s_x|\beta\rangle$ we get:

$$s_x \;=\; -\frac{1}{\sqrt{2}}(s_+ - s_-)$$

$$s_x|\beta\rangle \;=\; -\frac{1}{\sqrt{2}}(s_+|\beta\rangle - s_-|\beta\rangle)$$

$$=\; -\frac{1}{\sqrt{2}}(s_+|\beta\rangle)$$

$$=\; -\frac{1}{\sqrt{2}}\left(-\frac{1}{\sqrt{2}}|\alpha\rangle)\right)$$

$$=\; \frac{1}{2}|\alpha\rangle \tag{4.62}$$

Likewise, we get the following relations:

$$s_y|\beta\rangle \;=\; -\frac{i}{2}|\alpha\rangle \tag{4.63}$$

$$s_x|\alpha\rangle \;=\; \frac{1}{2}|\beta\rangle \tag{4.64}$$

$$s_y|\alpha\rangle \;=\; -\frac{i}{2}|\beta\rangle \tag{4.65}$$

and thus we get the spin matrices in the basis α, β:

$$\mathbf{s_x} \;=\; \begin{pmatrix} \langle\alpha|s_x|\alpha\rangle & \langle\alpha|s_x|\beta\rangle \\ \langle\beta|s_x|\alpha\rangle & \langle\beta|s_x|\beta\rangle \end{pmatrix}$$

$$=\; \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{4.66}$$

$$\mathbf{s_y} \;=\; \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \tag{4.67}$$

For s_z, we use

$$s_z |\Psi_{s,s_z}\rangle = s_z |\Psi_{s,s_z}\rangle \tag{4.68}$$

Therefore,

$$\mathbf{s_z} = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{4.69}$$

Using these results, we proceed to the representation of SOC in the basis $\{\Phi_l\}$ = $\{p_{-1}\alpha, \ p_0\alpha, \ p_1\alpha, \ p_{-1}\beta, p_0\beta, \ p_1\beta \ \}$. For the matrix elements of $l_z s_z$, for example:

$$\mathbf{l_z} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

and

$$\mathbf{s_z} = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

yield

$$
\mathbf{l_z s_z} = \left(
\begin{array}{ccc|ccc}
\langle p_{-1}\alpha|l_z s_z|p_{-1}\alpha\rangle & \langle p_{-1}\alpha|l_z s_z|p_0\alpha\rangle & \langle p_{-1}\alpha|l_z s_z|p_1\alpha\rangle & \langle p_{-1}\alpha|l_z s_z|p_{-1}\beta\rangle & \langle p_{-1}\alpha|l_z s_z|p_0\beta\rangle & \langle p_{-1}\alpha|l_z s_z|p_1\beta\rangle \\
\langle p_0\alpha|l_z s_z|p_{-1}\alpha\rangle & \langle p_0\alpha|l_z s_z|p_0\alpha\rangle & \langle p_0\alpha|l_z s_z|p_1\alpha\rangle & \langle p_0\alpha|l_z s_z|p_{-1}\beta\rangle & \langle p_0\alpha|l_z s_z|p_0\beta\rangle & \langle p_0\alpha|l_z s_z|p_1\beta\rangle \\
\langle p_1\alpha|l_z s_z|p_{-1}\alpha\rangle & \langle p_1\alpha|l_z s_z|p_0\alpha\rangle & \langle p_1\alpha|l_z s_z|p_1\alpha\rangle & \langle p_1\alpha|l_z s_z|p_{-1}\beta\rangle & \langle p_1\alpha|l_z s_z|p_0\beta\rangle & \langle p_1\alpha|l_z s_z|p_1\beta\rangle \\
\hline
\langle p_{-1}\beta|l_z s_z|p_{-1}\alpha\rangle & \langle p_{-1}\beta|l_z s_z|p_0\alpha\rangle & \langle p_{-1}\beta|l_z s_z|p_1\alpha\rangle & \langle p_{-1}\beta|l_z s_z|p_{-1}\beta\rangle & \langle p_{-1}\alpha|l_z s_z|p_0\beta\rangle & \langle p_{-1}\beta|l_z s_z|p_1\beta\rangle \\
\langle p_0\beta|l_z s_z|p_{-1}\alpha\rangle & \langle p_0\beta|l_z s_z|p_0\alpha\rangle & \langle p_0\beta|l_z s_z|p_1\alpha\rangle & \langle p_0\beta|l_z s_z|p_{-1}\beta\rangle & \langle p_0\alpha|l_z s_z|p_0\beta\rangle & \langle p_0\beta|l_z s_z|p_1\beta\rangle \\
\langle p_1\beta|l_z s_z|p_{-1}\alpha\rangle & \langle p_1\beta|l_z s_z|p_0\alpha\rangle & \langle p_1\beta|l_z s_z|p_1\alpha\rangle & \langle p_1\beta|l_z s_z|p_{-1}\beta\rangle & \langle p_1\alpha|l_z s_z|p_0\beta\rangle & \langle p_1\beta|l_z s_z|p_1\beta\rangle
\end{array}
\right)
$$

$$
= \left(
\begin{array}{cc|cc}
\left(
\begin{array}{ccc}
\langle p_{-1}\alpha|l_z|p_{-1}\alpha\rangle & \langle p_{-1}\alpha|l_z|p_0\alpha\rangle & \langle p_{-1}\alpha|l_z|p_1\alpha\rangle \\
\langle p_0\alpha|l_z|p_{-1}\alpha\rangle & \langle p_0\alpha|l_z|p_0\alpha\rangle & \langle p_0\alpha|l_z|p_1\alpha\rangle \\
\langle p_1\alpha|l_z|p_{-1}\alpha\rangle & \langle p_1\alpha|l_z|p_0\alpha\rangle & \langle p_1\alpha|l_z|p_1\alpha\rangle
\end{array}
\right) \langle\alpha|s_z|\alpha\rangle
&
\left(
\begin{array}{ccc}
\langle p_{-1}\alpha|l_z|p_{-1}\beta\rangle & \langle p_{-1}\alpha|l_z|p_0\beta\rangle & \langle p_{-1}\alpha|l_z|p_1\beta\rangle \\
\langle p_0\alpha|l_z|p_{-1}\beta\rangle & \langle p_0\alpha|l_z|p_0\beta\rangle & \langle p_0\alpha|l_z|p_1\beta\rangle \\
\langle p_1\alpha|l_z|p_{-1}\beta\rangle & \langle p_1\alpha|l_z|p_0\beta\rangle & \langle p_1\alpha|l_z|p_1\beta\rangle
\end{array}
\right) \langle\alpha|s_z|\beta\rangle \\
\hline
\left(
\begin{array}{ccc}
\langle p_{-1}\beta|l_z|p_{-1}\alpha\rangle & \langle p_{-1}\beta|l_z|p_0\alpha\rangle & \langle p_{-1}\beta|l_z|p_1\alpha\rangle \\
\langle p_0\beta|l_z|p_{-1}\alpha\rangle & \langle p_0\beta|l_z|p_0\alpha\rangle & \langle p_0\beta|l_z|p_1\alpha\rangle \\
\langle p_1\beta|l_z s_z|p_{-1}\alpha\rangle & \langle p_1\beta|l_z s_z|p_0\alpha\rangle & \langle p_1\beta|l_z s_z|p_1\alpha\rangle
\end{array}
\right) \langle\beta|s_z|\alpha\rangle
&
\left(
\begin{array}{ccc}
\langle p_{-1}\beta|l_z|p_{-1}\beta\rangle & \langle p_{-1}\alpha|l_z|p_0\beta\rangle & \langle p_{-1}\beta|l_z|p_1\beta\rangle \\
\langle p_0\beta|l_z|p_{-1}\beta\rangle & \langle p_0\alpha|l_z|p_0\beta\rangle & \langle p_0\beta|l_z|p_1\beta\rangle \\
\langle p_1\beta|l_z|p_{-1}\beta\rangle & \langle p_1\alpha|l_z|p_0\beta\rangle & \langle p_1\beta|l_z|p_1\beta\rangle
\end{array}
\right) \langle\beta|s_z|\beta\rangle
\end{array}
\right)
\tag{4.70}
$$

$$
l_z s_z = \frac{1}{2} \left(\begin{array}{ccc|ccc}
-1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 \\
\hline
0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & -1
\end{array} \right) \tag{4.71}
$$

$$ \tag{4.72} $$

Likewise, from

$$
l_x = \frac{1}{\sqrt{2}} \left(\begin{array}{ccc}
0 & 1 & 0 \\
1 & 0 & 1 \\
0 & 1 & 0
\end{array} \right) \tag{4.73}
$$

$$
s_x = \frac{1}{2} \left(\begin{array}{cc}
0 & 1 \\
1 & 0
\end{array} \right) \tag{4.74}
$$

we obtain

$$
l_x s_x = \frac{1}{2} \left(\begin{array}{ccc|ccc}
0 & 0 & 0 & 0 & \frac{1}{\sqrt{2}} & 0 \\
0 & 0 & 0 & \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\
0 & 0 & 0 & 0 & \frac{1}{\sqrt{2}} & 0 \\
\hline
0 & \frac{1}{\sqrt{2}} & 0 & 0 & 0 & 0 \\
\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} & 0 & 0 & 0 \\
0 & \frac{1}{\sqrt{2}} & 0 & 0 & 0 & 0
\end{array} \right) \tag{4.75}
$$

Similarly,

$$
l_y = \frac{i}{\sqrt{2}} \left(\begin{array}{ccc}
0 & 1 & 0 \\
-1 & 0 & 1 \\
0 & -1 & 0
\end{array} \right) \tag{4.76}
$$

$$
s_y = \frac{1}{2} \left(\begin{array}{cc}
0 & -i \\
i & 0
\end{array} \right) \tag{4.77}
$$

yield

$$\mathbf{l_y s_y} = \frac{1}{2} \left(\begin{array}{ccc|ccc} 0 & 0 & 0 & 0 & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & -\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & 0 & 0 & 0 & -\frac{1}{\sqrt{2}} & 0 \\ \hline 0 & -\frac{1}{\sqrt{2}} & 0 & 0 & 0 & 0 \\ \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & 0 & 0 & 0 & 0 \end{array} \right) \tag{4.78}$$

Finally, from

$$\mathbf{ls} = l_x s_x + l_y s_y + l_z s_z \tag{4.79}$$

we obtain the complete matrix for spin-orbit coupling in the basis $p_{-1}\alpha$, $p_0\alpha$, $p_1\alpha$, $p_{-1}\beta$, $p_0\beta$, $p_1\beta$:

$$\mathbf{ls} = \left(\begin{array}{ccc|ccc} -1 & 0 & 0 & 0 & \sqrt{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & \sqrt{2} \\ 0 & 0 & 1 & 0 & 0 & 0 \\ - & - & - & - & - & - \\ 0 & 0 & 0 & 1 & 0 & 0 \\ \sqrt{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & \sqrt{2} & 0 & 0 & 0 & -1 \end{array} \right) \tag{4.80}$$

4.4.1.1   Application to the Molecular VB-Wavefunctions

Because the basis for the model Hamiltonian consists of the 36 molecular VB-wavefunctions (eqn. 4.1, table 4.1, section 4.2), we have to apply the matrices for the atomic wavefunctions to the molecular wavefunctions to get a representation that can be added to the system's Hamiltonian. For this purpose we use the relation derived in section 4.4:

$$V_{SO} = \Delta_a \mathbf{l_a s_a} + \Delta_b \mathbf{l_b s_b}$$

with a denoting the F atom and b the Cl atom.

$$\langle \Psi_i | \Delta_a \underbrace{\sum_i \mathbf{l_i s_i}}_{a} + \Delta_b \underbrace{\sum_i \mathbf{l_i s_i}}_{b} | \Psi_j \rangle = \Delta_a \langle \Psi_i | \mathbf{l_1 s_1} + \mathbf{l_2 s_2} | \Psi_j \rangle_a + \Delta_b \langle \Psi_i | \mathbf{l_1 s_1} + \mathbf{l_2 s_2} | \Psi_j \rangle_b$$

$$\tag{4.81}$$

and

$$\Delta_a \langle \Psi_i | \mathbf{l_1 s_1 + l_2 s_2} | \Psi_j \rangle_a = \Delta_a \langle \Psi_i | \mathbf{l_1 s_1} | \Psi_j \rangle_a + \Delta_a \langle \Psi_i | \mathbf{l_2 s_2} | \Psi_j \rangle_a \qquad (4.82)$$

As can be seen from equation 4.8 and table 4.1, the molecular VB-wavefunctions $\Psi_i(1,2)$ are expressed in terms of atomic wavefunctions $\Phi_n(1)$, $\Phi_l(2)$ as follows:

$$\Psi_i(1,2) = \sum_k \sum_l c_{ikl} \Phi_k(1) \Phi_l(2) \qquad (4.83)$$

$$\Psi_j(1,2) = \sum_m \sum_n c_{jmn} \Phi_m(1) \Phi_n(2) \qquad (4.84)$$

The resulting spin-orbit matrix elements for a specific electron ("1") is, for example:

$$\langle \Psi_i | \mathbf{l_1 s_1} | \Psi_j \rangle = \sum_k \sum_l \sum_m \sum_n c_{ikl} c_{jmn} \langle \Phi_k(1) \Phi_l(2) | \mathbf{l_1 s_1} | \Phi_m(1) \Phi_n(2) \rangle$$

$$= \sum_k \sum_l \sum_m \sum_n c_{ikl} c_{jmn} \underbrace{\langle \Phi_l(2) | \Phi_n(2) \rangle}_{\delta_{ln}} \underbrace{\langle \Phi_k(1) | \underbrace{\mathbf{l_1 s_1} | \Phi_m(1) \rangle}_{apply}}_{integrate}$$

As a consequence, the total spin-orbit matrix element is, in general,

$$\langle \Psi_i(1,2) | \Delta_a \underbrace{\sum_i \mathbf{l_i s_i}}_{a} + \Delta_b \underbrace{\sum_i \mathbf{l_i s_i}}_{b} | \Psi_j(1,2) \rangle =$$

$$\sum_k \sum_l \sum_m \sum_n c_{ikl} c_{jmn} \big(\Delta_a [\langle \Phi_l(2) | \Phi_n(2) \rangle \langle \Phi_k(1) | \mathbf{l_i s_i} | \Phi_m(1) \rangle_a + \langle \Phi_k(1) | \Phi_m(1) \rangle \langle \Phi_l(2) | \mathbf{l_2 s_2} | \Phi_n(2) \rangle_a]$$

$$+ \Delta_b [\langle \Phi_l(2) | \Phi_n(2) \rangle \langle \Phi_k(1) | \mathbf{l_i s_i} | \Phi_m(1) \rangle_b + \langle \Phi_k(1) | \Phi_m(1) \rangle \langle \Phi_l(2) | \mathbf{l_2 s_2} | \Phi_n(2) \rangle_b] \big)$$

$$(4.85)$$

4.4.1.2 Example

As an explicit example the matrix element

$$\langle {}^1\Sigma(1,2) | \sum_i \Delta_a \underbrace{\mathbf{l_i s_i}}_{a} + \sum_i \Delta_b \underbrace{\mathbf{l_i s_i}}_{b} | {}^3\Pi(1,2) \rangle$$

with

$$
\begin{aligned}
{}^1\Sigma &= \frac{1}{\sqrt{2}}(a_0(1)b_0(2) + b_0(1)a_0(2))\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2)) \\
&= \frac{1}{2}(a_0(1)\alpha(1)b_0(2)\beta(2) + b_0(1)\alpha(1)a_0(2)\beta(2) - a_0(1)\beta(1)b_0(2)\alpha(2) - b_0(1)\beta(1)a_0(2)\alpha(2)) \\
{}^3\Pi &= \frac{1}{2}((a_0(1)b_+(2) - b_+(1)a_0(2)) - (a_+(1)b_0(2) - b_0(1)a_+(2)))(\beta(1)\beta(2)) \\
&= \frac{1}{2}[a_0(1)\beta(1)b_+(2)\beta(2) - b_+(1)\beta(1)a_0(2)\beta(2) - a_+(1)\beta(1)b_0(2)\beta(2) \\
&\quad + b_0(1)\beta(1)a_+(2)\beta(2)]
\end{aligned}
$$

is evaluated as follows, First $l_1 s_1$ is only operating on the part of each expression which belongs to electron (1).

$$
\mathbf{ls} = \left(
\begin{array}{ccc|ccc|l}
 & p_{-1}\alpha & p_0\alpha & p_1\alpha & p_{-1}\beta & p_0\beta & p_1\beta & \\
\hline
 & -1 & 0 & 0 & 0 & \sqrt{2} & 0 & p_{-1}\alpha \\
 & 0 & 0 & 0 & 0 & 0 & \sqrt{2} & p_0\alpha \\
 & 0 & 0 & 1 & 0 & 0 & 0 & p_1\alpha \\
\hline
 & 0 & 0 & 0 & 1 & 0 & 0 & p_{-1}\beta \\
 & \sqrt{2} & 0 & 0 & 0 & 0 & 0 & p_0\beta \\
 & 0 & \sqrt{2} & 0 & 0 & 0 & -1 & p_1\beta
\end{array}
\right)
$$

From this we can see that $l_1 s_1$ operating for example on $a_0(1)\beta(1) = p_o(1)\beta(1)$ will give $\sqrt{2}a_-(1)\alpha(1) = \sqrt{2}p_-(1)\alpha(1)$. Similarly, $l_1 s_1$ operating on $a_+(1)\beta(1)$ gives $\sqrt{2}p_0(1)\alpha(1) - p_1(1)\beta(1)$

Similar operations on all atomic basis functions which sontribute to ${}^3\Pi(1,2)$ yield

$$
\begin{aligned}
l_1 s_1 |{}^3\Pi(1,2)\rangle_a &= \frac{1}{2}[\sqrt{2}a_-(1)\alpha(1)b_+(2)\beta(2) - b_+(1)\beta(1)a_0(2)\beta(2) - \sqrt{2}a_0(1)\alpha(1)b_0(2)\beta(2) \\
&\quad + a_+(1)\beta(1)b_0(2)\beta(2) + b_0(1)\beta(1)a_+(2)\beta(2)]
\end{aligned}
$$

Finally, the $l_1 s_1$ matrix element of $^1\Sigma(1,2)$ on $^3\Pi(1,2)$ is evaluated as

$$\langle ^1\Sigma(1,2)|\mathbf{l_1 s_1}|^3\Pi(1,2)\rangle_a \;=$$

$$\langle \frac{1}{2}(a_0(1)\alpha(1)b_0(2)\beta(2) + b_0(1)\alpha(1)a_0(2)\beta(2) - a_0(1)\beta(1)b_0(2)\alpha(2)$$

$$-b_0(1)\beta(1)a_0(2)\alpha(2))|\frac{1}{2}(\sqrt{2}a_-(1)\alpha(1)b_+(2)\beta(2) - b_+(1)\beta(1)a_0(2)\beta(2)$$

$$-\sqrt{2}a_0(1)\alpha(1)b_0(2)\beta(2) + a_+(1)\beta(1)b_0(2)\beta(2) + b_0(1)\beta(1)a_+(2)\beta(2))\rangle$$

$$\begin{aligned}
=\;& \frac{1}{4}[\langle a_0(1)\alpha(1)|\sqrt{2}a_-(1)\alpha(1)\rangle\langle b_0(2)\beta(2)|b_+(2)\beta(2)\rangle \\
&- \langle a_0(1)\alpha(1)|b_+(1)\beta(1)\rangle\langle b_0(2)\beta(2)|a_0(2)\beta(2)\rangle \\
&- \langle a_0(1)\alpha(1)|\sqrt{2}a_0(1)\alpha(1)\rangle\langle b_0(2)\beta(2)|b_0(2)\beta(2)\rangle \\
&+ \langle a_0(1)\alpha(1)|a_+(1)\beta(1)\rangle\langle b_0(2)\beta(2)|b_0(2)\beta(2)\rangle \\
&+ \langle a_0(1)\alpha(1)|b_0(1)\beta(1)\rangle\langle b_0(2)\beta(2)|a_+(2)\beta(2)\rangle \\
&+ \langle b_0(1)\alpha(1)|\sqrt{2}a_-(1)\alpha(1)\rangle\langle a_0(2)\beta(2)|b_+(2)\beta(2)\rangle \\
&- \langle b_0(1)\alpha(1)|b_+(1)\beta(1)\rangle\langle a_0(2)\beta(2)|a_0(2)\beta(2)\rangle \\
&- \langle b_0(1)\alpha(1)|\sqrt{2}a_0(1)\alpha(1)\rangle\langle a_0(2)\beta(2)|b_0(2)\beta(2)\rangle \\
&+ \langle b_0(1)\alpha(1)|a_+(1)\beta(1)\rangle\langle a_0(2)\beta(2)|b_0(2)\beta(2)\rangle \\
&+ \langle b_0(1)\alpha(1)|b_0(1)\beta(1)\rangle\langle a_0(2)\beta(2)|a_+(2)\beta(2)\rangle \\
&- \langle a_0(1)\beta(1)|\sqrt{2}a_-(1)\alpha(1)\rangle\langle b_0(2)\alpha(2)|b_+(2)\beta(2)\rangle \\
&+ \langle a_0(1)\beta(1)|b_+(1)\beta(1)\rangle\langle b_0(2)\alpha(2)|a_0(2)\beta(2)\rangle \\
&+ \langle a_0(1)\beta(1)|\sqrt{2}a_0(1)\alpha(1)\rangle\langle b_0(2)\alpha(2)|b_0(2)\beta(2)\rangle \\
&- \langle a_0(1)\beta(1)|a_+(1)\beta(1)\rangle\langle b_0(2)\alpha(2)|b_0(2)\beta(2)\rangle \\
&+ \langle a_0(1)\beta(1)|b_0(1)\beta(1)\rangle\langle b_0(2)\alpha(2)|a_+(2)\beta(2)\rangle \\
&- \langle b_0(1)\beta(1)|\sqrt{2}a_-(1)\alpha(1)\rangle\langle a_0(2)\alpha(2)|b_+(2)\beta(2)\rangle \\
&+ \langle b_0(1)\beta(1)|b_+(1)\beta(1)\rangle\langle a_0(2)\alpha(2)|a_0(2)\beta(2)\rangle \\
&+ \langle b_0(1)\beta(1)|\sqrt{2}a_0(1)\alpha(1)\rangle\langle a_0(2)\alpha(2)|b_0(2)\beta(2)\rangle \\
&- \langle b_0(1)\beta(1)|a_+(1)\beta(1)\rangle\langle a_0(2)\alpha(2)|b_0(2)\beta(2)\rangle \\
&+ \langle b_0(1)\beta(1)|b_0(1)\beta(1)\rangle\langle a_0(2)\alpha(2)|a_+(2)\beta(2)\rangle \\
=\;& \frac{1}{4}[-\sqrt{2}\langle a_0(1)\alpha(1)|a_0(1)\alpha(1)\rangle\langle b_0(2)\beta(2)|b_0(2)\beta(2)\rangle] \\
=\;& -\frac{1}{4}\sqrt{2}
\end{aligned}$$

Similar to this procedure we get for $\mathbf{l_2s_2}$

$$
\begin{aligned}
\langle^1\Sigma(1,2)|\mathbf{l_2s_2}|^3\Pi(1,2)\rangle_a &= \frac{1}{4}[-\sqrt{2}\langle b_0\,(1)\beta(1)|b_0(1)\beta(1)\rangle\langle a_0(2)\alpha(2)|a_0(2)\alpha(2)\rangle] \\
&= -\frac{1}{4}\sqrt{2}
\end{aligned}
$$

So for the total matrix element:

$$
\begin{aligned}
\langle^1\Sigma(1,2)|\Delta_a(\mathbf{l_1s_1}+\mathbf{l_2s_2})|^3\Pi(1,2)\rangle_a &= 2\cdot(-\frac{1}{4}\sqrt{2})\Delta_a \\
&= -\frac{1}{\sqrt{2}}\Delta_a \\
\langle^1\Sigma(1,2)|\Delta_b(\mathbf{l_1s_1}+\mathbf{l_2s_2})|^3\Pi(1,2)\rangle_b &= -\frac{1}{\sqrt{2}}\Delta_b \\
\Rightarrow\ \langle^1\Sigma(1,2)|\mathbf{V_{SO}}|^3\Pi(1,2)\rangle &= -\frac{1}{\sqrt{2}}(\Delta_a+\Delta_b)
\end{aligned}
$$

All 36x36 matrix elements are calculated by means of the same technique and the resulting values are added as off-diagonal elements to the system Hamiltonian.

4.4.2 Electron-Hole Dualism

To show that this approach is valid, one has to prove that a shell occupied by n electrons, leads to the same (L,S)-terms like a shell occupied with (g-n) holes with g corresponding to the degeneracy. So the configuration with n electrons is equivalent to a configuration with (g-n) occupied holes.

$$
\overset{Microstates}{} \qquad\qquad\qquad \overset{Microstates}{}
$$
$$
n - electrons \;=\; \begin{pmatrix} g \\ n \end{pmatrix} \;=\; \begin{pmatrix} g \\ g-n \end{pmatrix} \;=\; (g-n) - holes
$$

For each (M_S, M_L)-microstate for n electrons there is one $(-M_S, -M_L)$-microstate with (g-n) holes. For example, by comparing the p^1 and p^5 configuration of an atom, in the former there is one microstate with M_L equals to +1 and M_S equals to $+\frac{1}{2}$ for the one hole. Let us denote this state as 1^+ with the digit corresponding to the value of M_L and the index corresponding to spin $+\frac{1}{2}$. If we would have p^5 configuration, there will be one configuration where the hole will be located at M_L equals to +1 and M_S equals to $+\frac{1}{2}$ and the five electrons inhabiting the microstates $1^-, 0^+, 0^-, -1^+$ and -1^-, which leads to the corresponding microstate with M_L equals -1 and M_S $-\frac{1}{2}$. This will be the case for all of the

microstates of the p^1 configuration.

A ^{2S+1}L-term consists of (M_L, M_S)-states with

$$M_L = L, L - 1, L - 2... - L$$

$$M_S = S, S - 1, S - 2... - S$$

so for each (M_L, M_S)-electronstate one $(-M_L, -M_S)$-holestate will be included. So we can conclude that a state with n electrons leads to the same (L,S)-terms as a state with (g-n)- electrons, only with a change in sign for the coupling elements.